AN OVERVIEW OF RESID CHARACTERIZATION BY MASS SPECTROMETRY AND SMALL ANGLE SCATTERING TECHNIQUES

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ABSTRACT

The purpose of this presentation is to discuss what is known about the molecular structures found in petroleum resid from mass spectrometry and small angle neutron and X-ray scattering methods. The question about molecular size distributions and the occurrence of aggregation in the asphaltene fraction will be examined. Our understanding of this problem has evolved with the application of new analytical methods. Also, correlations with results from other approaches will be discussed. In addition, the issue of the nature of the heteroatom-containing molecules will be examined and the challenges that remain in this area.

INTRODUCTION

As light crudes disappear, there is a need to process heavier crudes with increasing amounts of resid. Petroleum resids can be fractionated by solubility with asphaltenes, the heptane insoluble fraction being the greatest problem in upgrading processing. This fraction is more aromatic than any of the other fractions and contains much of the heteroatoms and metals. Speciation of asphaltenes is extremely difficult and even measuring an accurate molecular weight distribution is problematic. As more is learned about the nature of petroleum asphaltenes, their apparent molecular weights are being lowered. Much of this information is the result of mass spectrometric and small angle X-ray and neutron scattering measurements. These studies suggest that asphaltenes are comprised of molecules with molecular weights less than 1500 and typically are aggregated even in high temperature processing.

Mass Spectrometry

Because of the low volatility of the various components of resid, direct thermal or laser desorption in the MS source has been the most successful MS method to characterize these complex mixtures. Various MS methods have been used including: field ionization mass spectrometry (FIMS), low-voltage (LVMS) and chemical ionization (CIMS), laser desorption mass spectrometry (LDMS), and high resolution mass spectrometry (HRMS).

Some of the first work using this method was reported by Boduszynski, who described a multistep separation followed by characterization of a series of atmospheric resids. The volatile fractions were separated by vacuum distillation and the non-distillable fraction was separated by a sequential elution fractionation (SEF).[1] FIMS data was shown for one of the suite of separation fractions. The mass ranges broaden with succession fractions and the average molecular mass increased until they reached the first SEF fraction, then there was a decrease in subsequent fraction. It was stated that the mass distribution varied with the petroleum source. No significant amount of ions were observed at over a mass of 1900. Although no data was shown, it was stated that field desorption MS gave similar results to FIMS. A more recent FIMS study looked at high molecular weight hydrocarbons from a crude oil and solid bitumen.[2] Several series of hydrocarbons up to C_{110} were observed, which corresponds to an upper mass of ~1500, consistent with what has been seen in other studies.

A Middle East vacuum resid was separated by solubility into four fractions: pentane soluble oil, heptane soluble pentane insoluble resins, cyclohexane soluble/heptane insoluble asphaltenes [1], and cyclohexane insoluble asphaltenes [2].[3] These fractions were analyzed by thermal volatilization (50-300 °C), low voltage low resolution, mass spectrometry (triple quadrupole MS). The measured average mass decreased within the series: oil (615), resin (485), asphaltene 1 (440) and asphaltene 2 (410). Also, the yields from the thermolysis decreased with an increase in the series and they speculated that upper bounds molecular mass may be higher. However, since the FIMS data showed the same trends, the relative ratios of molecular weights between the fractions may not change even if the entire sample was ionized. CIMS gave similar results to the low voltage experiment.

Although HRMS has been one of the methods of choice for characterizing volatile petroleum fractions, it has only more recently been applied to the complex polar resid fractions.[4,5] In the HRMS studies, the samples were desorbed from a high temperature probe that was heated from 200-700 °C. Quantitative experiments showed that >95% of the samples, even the asphaltenes, were desorbed. In both HRMS and LDMS, the oil samples gave a larger average molecular weight[5] distribution compared to the asphaltene samples. This was also the case in the comparison of a non-colloidal (soxhlet extractable) asphaltene. However, the size of the aromatic rings were larger for the asphaltene compared to the oil, as seen in Figure 1. From HRMS data, formulae can be calculated that can yield the type of data shown in Figure 1. The oil, aromatic cores, contained on an average, longer aliphatic side chains that increased the average molecular weight and decreased the tendency for forming colloids. Also, the yield of heteroatom containing molecules was much greater for the asphaltene, as is shown for sulfur in Figure 1.

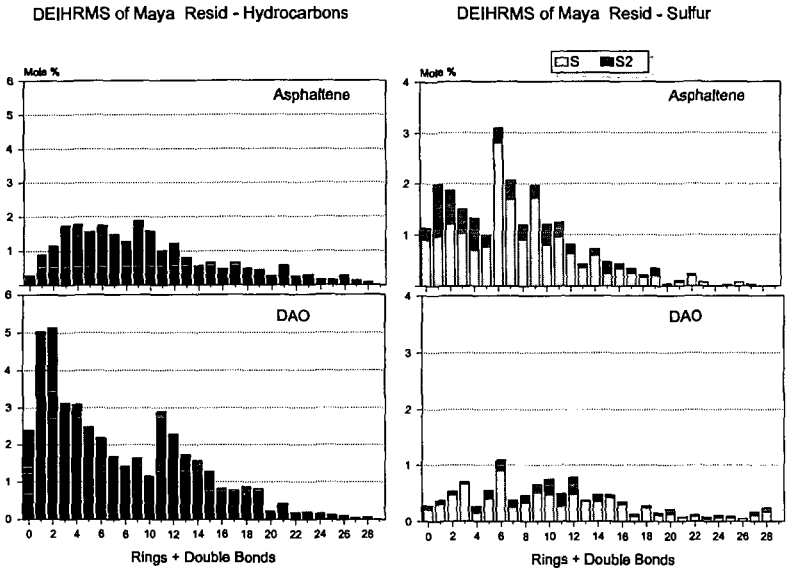


Figure 1. Double bond equivalent distributions for hydrocarbons and sulfur compounds from DEIHRMS analysis.

Small Angle Scattering

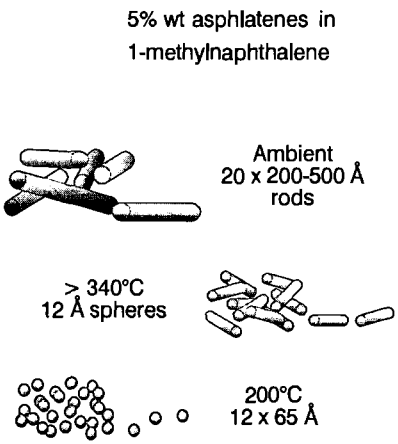
Using small angle X-ray and neutron scattering methods, the nature of disordered materials over length scales of 6-6000 Å can be observed. Depending on the system, the methods can provide information on molecular or particle size, shape, and surface properties. X-rays scatter off electrons, which are z number dependent phenomena, while neutrons scatter off the nucleus and are dependent on the scattering length density, which can even vary between isotopes such as hydrogen and deuterium.

Initial studies using SAXS suggest that vacuum resid asphaltene particles dispersed in resid oil are spherical aggregates that range in radii from 30-60 Å with a polydispersity of 15-20%, depending on the petroleum source.[6] Using SANS, it has been shown that the size of the asphaltene aggregates do not change with variation of solvent composition for toluene/pyridine mixtures and concentrations of asphaltene in solution. However, from SANS analyses of coal pyridine extracts, it has been shown that pyridine is not a good solvent for complex polar mixtures and does not yield true solutions.[7]

Maya-derived asphaltenes were studied by SANS in d_{10}-1-methylnaphthalene from 20-400 °C. Using a modified Guinier analysis, it was shown that the colloidal materials were rod-shaped at the lower temperatures.[8] These rod-shaped particles had a fairly uniform radius but were polydispersed in length. At high temperature, spherical particles formed resulting in uniform 12 Å spheres at 400 °C. Scheme 1 depicts changes in particle shape and size with temperature. The changes at high

temperature were irreversible and secondary density with covalent bond formation probably occurred. The oils were non-aggregated and showed no scattering.

SCHEME 1



Also using SANS, it was found that the size of the colloidal asphaltene particles decreasing with heating as with increasing with dilution with resin material, and increase with the addition of n-hexane.[9] Apparently resin makes a better solvent than pyridine. Recently, the age hardening of resin was followed by both SAXS and SANS.[10] The asphaltene macrostructure appears not to change with aging and the major effect is the changes in the maltenes.

CONCLUSIONS

From MS and small angle scattering studies, it is apparent that petroleum asphaltenes are colloidal in nature even in "good" solvents and at high temperatures. They are not large polycyclic aromatics, but instead have a maximum ring number of typically 10-11, with the average being 5-6. Asphaltenes are rich in heteroaromatic compounds.

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